PATENT SPECIFICATION 1,090,971

DRAWINGS ATTACHED.

Inventors:—PAUL IVAN WILSON and FRANK ROY JOHNSTON.

1,090,971

Date of filing Complete Specification: Jan. 22, 1965.

Application Date: Feb. 12, 1964. No. 5787/64.

Complete Specification Published: Nov. 15, 1967.

Index at Acceptance:—**C1** A(K9B, N34); **B1** B3C; **B2** F(6B, 19); **B2** K(1C1, 3C, 3D, 7BX, 8G, 9C, 9Q1, 9Q2, 9Q5, 9Q6, 9QY); **C3** F(2H, 3E, 4); **C3** P(4A, 4C6B, 4C12A, 4C14B, 4C16A, 4C16C, 4D3B1, 4S3).

Int. Cl.:—B 05 c 3/02 //B 01 d, B 05 b, C 08 b, f.

COMPLETE SPECIFICATION.

Method and Apparatus for Producing Microencapsulated Particles.

We, THE DUNLOP COMPANY LIMITED, formerly Dunlop Rubber Company Limited, a British Company, of 1, Albany Street, London, N.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for producing microencapsulated particles. By the phrase "microencapsulated particles" we mean microscopic particles having a diameter in the range 0.01 to 100 microns each of which is individually provided with a sheath of a polymeric or resinous material over at least 50% of its surface. For certain end uses it is particularly preferred that each particle should have a sheath over 100% of its surface.

According to the present invention a method of producing microencapsulated particles of a solid substance comprises sub-dividing into droplets a feedstock comprising either a solution of a film-forming thermoplastic polymeric or resinous material in a volatile organic liquid having the said solid substance dispersed and/or dissolved therein or a dispersion in a liquid dispersing medium of such a solution and causing said droplets to contact steam in a treatment zone so that the droplets are intimately mixed with steam and steam condenses on the droplets thereby volatilizing said organic liquid whilst the droplets are free of external contact with a solid or bulk liquid, the steam being supplied to the treatment zone from a source which is independent of the treatment zone.

Generally the feedstock is sub-divided into droplets by mechanical means and the droplets are subsequently passed into steam. It is possible, however, in some circumstances to atomise the feedstock by means of a jet of steam, in which case atomisation and mixing of the droplets with steam occur simultaneously. This method has been found to be effective when the feedstock is a dispersion in water of a solution.

Preferably the feedstock is a solution having microscopic particles of the solid substance dispersed therein, but the solid substance may be partly or wholly soluble in the solution in which cases the solid substance will be partly dispersed and partly dissolved in the solution and wholly dissolved in the solution respectively.

The method of the present invention may be carried out in apparatus comprising means for sub-dividing a feedstock into droplets and passing said droplets into steam and means for supplying the steam into which said droplets pass and means for collecting a solid product.

By a "solid substance" we mean a substance which is solid at ambient temperatures. The phrase "bulk liquid" as used in this specification does not include water which is present on the surface of each droplet due to condensation of steam. The word "stiff" is used in this specification to describe solid material which does not flow into spaces around or within the body formed by the material and which does not coalesce with similar material in other bodies adjacent to said body.

The portion of each droplet remaining after volatilization of the solvent is collected

in a suitable manner. If the thermoplastic polymeric or resinous material is stiff at the temperature at which collection is carried out (which is normally ambient temperature), the product may be collected in a liquid or on a solid surface. The product in this case is normally discrete solid microencapsulated particles which may be removed and dried in bulk. However, if the thermoplastic polymeric or resinous material is not stiff at the temperature at which collection is carried out the product is normally collected in water in the presence of a surface active agent. The surface active agent may be present in the product and/or the water. The product in this case is normally discrete microencapsulated particles which must be kept dispersed in water if they are not to coalesce.

The thermoplastic polymeric or resinous material must be capable of forming a film at a temperature above 50°C. in the presence of a small proportion of organic liquid.

The thermoplastic polymeric or resinous material is preferably water-insoluble. Preferably the thermoplastic polymeric or resinous material is substantially inert towards the solid substance whose particles are to be microencapsulated. Among suitable polymeric materials are cellulose nitrate, polycarbonate, poly(vinyl acetate), ethyl cellulose, polypropylene, polyethylene and polystyrene.

The steam may suitably be superheated to a limited extent provided that some of it condenses on the droplets.

The feedstock must be of sufficiently low viscosity to allow satisfactory sub-division into droplets.

The volatile organic liquid may be one or more aromatic or aliphatic hydrocarbons, chlorinated hydrocarbons, esters, ketones, or ethers which are solvents for the thermoplastic polymeric or resinous material. Examples of such solvents are toluene, n-heptane, chloroform, chlorobenzene, carbon tetrachloride, trichlorethylene, ethyl acetate and acetone.

Volatilization of the organic liquid in the presence of steam will occur at temperatures below the "boiling point" of the liquid which is measured in air at atmospheric pressure. An organic liquid which has a reasonably low latent Heat of Volatilization may be volatilized in steam at 100°C although the boiling point of the liquid is substantially in excess of 100°C. e.g. 130°C. However, the vapour of a liquid having a very high boiling point may form only a small part of an equilibrium mixture with steam, and once equilibrium has been reached volatilization may be inhibited. The successful operation of the invention will depend inter alia on the latent heat of volatilization of the organic liquid and the steam pressure; therefore no upper limit of boiling point can be given for the volatile organic liquids which can be volatilized by the present method. However, the method has been found particularly effective for organic liquids having a boiling point in air below 100°C.

If the thermoplastic polymeric or resinous material is stiff at ambient temperatures it is preferred to use as the organic liquid a mixture of solvents at least one of which has a high boiling point i.e. above 100°C. Such a high boiling solvent acts as a plasticiser and tends to inhibit the formation of hollow portions in the thermoplastic polymeric or resinous material.

If the feedstock is a dispersion, the dispersing medium may be water or a further liquid organic substance which is substantially immiscible with the organic liquid referred to above and in which the thermoplastic polymeric or resinous material is substantially insoluble.

Preferably, when the solid substance is dispersed in the solution of the thermoplastic polymeric or resinous material the rate of sub-division of the feedstock into droplets is such that one particle of solid substance from the dispersion is included in each droplet. When the feedstock is a dispersion of a solution of the thermoplastic polymeric or resinous material, and the solid substance is dispersed in the solution then the solution is preferably dispersed as finely as possible to ensure that one particle of solid substance is included in each droplet.

The feedstock may be subdivided into droplets by any method of atomisation which produces a fine spray of uniform droplets. It is preferred to use a method of centrifugal atomisation for example by supplying the feedstock to the surface of a disc or inverted cup spinning at high speed. The feedstock is either broken directly into droplets at the edge of the disc, or filaments form at the edge of the disc and these break up, or a sheet is formed extending beyond the edge of the disc and this breaks up into filaments and eventually droplets. The behaviour during atomisation depends on a variety of factors such as the peripheral speed of the disc or cup, the rate of feed and feedstock properties such as viscosity and surface tension. Normally the disc or cup is rotated about a vertical axis so that the droplets are flung out in a horizontal spray. In an inverted cup atomiser the feedstock is supplied to the internal surface of the cup, possibly by a small auxiliary disc mounted within the cup.

Other possible methods of atomisation include impact atomisation. The simplest form of impact atomiser is a tube fed with feedstock under pressure and a suitably dis-

posed target plate, for example a circular plate at right angles to the axis of the tube, against which the feedstock is directed.

Generally the method of centrifugal atomisation is the most satisfactory for producing microencapsulated particles since it can produce very small droplets which have only one particle of the solid substance in each droplet.

It is essential for satisfactory operation of the invention that there should be intimate mixing of the droplets with steam in conditions which tend to draw the volatilized organic liquid away from the mixing zone. It has been found that satisfactory operation is achieved by "cross-current" mixing in which a spray of droplets is struck at approximately right angles by a jet of steam. If the atomiser throws out a horizontal spray of droplets, the steam source may suitably be arranged to supply a multiplicity of jets of steam vertically downwards close to the edge of the atomiser. In this case, the steam mixes intimately with the droplets and deflects them slightly downwards. Some of the steam condenses on the droplets and the remainder of the steam carries the volatilized organic liquid away from the mixing zone.

If the feedstock is a dispersion of a solution in water, the atomisation and mixing with steam may be achieved substantially simultaneously. An attenuated stream of feedstock fed under pressure may be broken up by contact with steam at high velocity. In an "internal" mixing arrangement, the steam contacts the feedstock inside a chamber and the resulting spray exits through a venturi orifice. In an "external" mixing arrangement, the steam and feedstock contact each other in the turbulent flow region outside a feedstock jet orifice. In operating these methods considerable care must be exercised if fine atomisation is to be achieved without excessive coagulation of the feedstock dispersion. The supply pipes for feedstock and steam must be kept apart as far as possible or adequate thermal insulation must be provided between them. These methods have not yet produced microencapsulated particles as small as those produced by a centrifugal-atomisation method.

The successful removal of the volatilized organic liquid from the mixing zone depends to some extent on maintenance of a pressure gradient from the relatively high pressure mixing zone to a relatively low pressure zone. With the method of the present invention it is not necessary to maintain the low pressure zone by mechanical means, such as a continuous vacuum pump. If the process is carried out in an open system in which the atomisation equipment is mounted in the atmosphere, a pressure gradient may be maintained by the diffusion of the vapour of the organic liquid into the atmosphere. In a partially closed system a pressure gradient may be maintained by an extraction fan mounted in working relationship to an exit from the system. It is desirable on grounds of safety, health and economics to condense the vapour of the organic liquid. It is therefore desirable to operate an enclosed system incorporating a condenser for the vapour. It has been found that in an enclosed system a pressure gradient may be maintained by continuous condensation in a suitable place of the vapour of the organic liquid and steam. For example a condenser may be arranged around the walls of the chamber in which volatilization takes place, or a separate condenser may be provided outside the chamber.

One effective form of condenser consists of an annular condensing column surrounding the upper part of the walls of the volatilization chamber, the condensing column being filled with fragments of pipeclay or similar material and having a stream of water descending over the fragments. The condensing column is open to atmosphere at the top and open to the volatilization chamber at the bottom. The vapour of the organic liquid and steam pass downwardly from the mixing zone to the bottom of the condensing column and then upwardly into the condensing column. Several other alternative forms of condenser are described by way of example with reference to the drawings below.

It is desirable to remove the product continuously from an enclosed system. In one suitable form of apparatus the product is collected in a funnel positioned beneath the atomisation equipment. The funnel may suitably be swept by a swirling stream of water. If the water is circulated in the system it will usually attain a temperature of about 85°C. which will help to prevent the vapour of the volatilised liquid condensing on the funnel.

In determining the conditions suitable for successful operation of this invention, the following factors in particular should be considered and balanced:—

1) The temperature and rate of supply of the steam.
2) The latent heat of evaporation and the boiling point of the organic liquid, or part of it.
3) The dimensions of the apparatus and the trajectory and size of the droplets.
4) The rate of supply of the feedstock.
5) The viscosity of the feedstock.
6) The film-forming properties of the polymeric or resinous material at elevated temperature in the presence of a small proportion of organic liquid.

The invention is normally applied to solid particles which do not suffer a change of state during the process, but the invention is also usefully applied to a solid substance which dissolves in the organic liquid and reprecipitates during volatilization of the organic liquid or to a solid substance which melts to a limited extent during the process. The invention is particularly usefully applied to particles of active rubber compounding ingredients such as vulcanization agents, accelerators, antioxidants, blowing agents, initiators and catalysts, for example sulphur, mercaptobenzthiazole, zinc diethyl dithiocarbamate, and paraformaldehyde. In microencapsulated particles of such ingredients, the sheath is adapted to expose the substantial part of the surface of each particle under predetermined conditions and/or adapted to permit the release of the ingredient if the said ingredient is fluid under predetermined conditions. The use of microencapsulated particles of such ingredients is described in our Applications Nos. 5791/64, 5789/64 and 5790/64 (Serial Nos. 1,090,974 1,090,972, 1,090,973), filed on even date herewith.

Preferably the particle diameter before microencapsulation is in the range of 1—10 microns.

If a polymeric or resinous material which is not stiff at the normal temperature of collection is used as a sheath material, the invention is useful for producing a dispersion containing microencapsulated particles of a pigment such as titanium dioxide.

The present invention provides a method of producing microencapsulated particles having sheaths of a much wider range of materials than has been possible heretofore. The invention has particular advantages for the production of microencapsulated particles of rubber compounding ingredients in that it can produce particles which may have sheaths capable of withstanding the conditions in which a rubber composition is prepared and processed. The success of the invention is believed to be derived from the use of condensable steam as the stripping gas in a spray volatilization process for the volatilization of an organic liquid. The condensable steam has a high heat content per unit volume and high availability for transfer of this heat. The heat requirement for volatilization of a volatile organic liquid is relatively low. Volatilization of the organic liquid is therefore very rapid, with the result that microencapsulated particles are formed during a relatively short free flight. The standard for comparison in these remarks is the known process for spray drying of aqueous solution using air as the stripping gas.

In a particularly suitable apparatus, the means for subdividing the feedstock into droplets consists of a horizontal spinning disc atomiser, capable of very high speeds. A feed pipe for the feedstock discharges above the atomiser disc. A steam distribution vessel is also mounted above the atomiser disc. This vessel has controlled heating means and has apertures in its lower surface for release of jets of steam.

Directly below the atomiser disc there are collecting means such as a tray or funnel or a trough of water.

In some embodiments of the apparatus, the atomiser is mounted near the top of a vertical cylindrical chamber having a height to diameter ratio of from 1:1 to 4:1.

The chamber may be provided with cooling surfaces or cold water sprays for condensation. Alternatively if the rate of supply of steam is sufficient and/or if the walls of the chamber are heated to inhibit condensation, a separate condenser may be used, the condenser being connected to the chamber by means of a duct. The two arrangements may be combined in such a way that only steam condenses in the chamber while steam and solvent vapour condense in the separate chamber.

In an alternative embodiment of the apparatus for experimental purposes when recovery of the solvent and condensation of the steam are not necessary, the atomiser and feed and steam supply equipment may be mounted openly in the atmosphere.

In using the apparatus described above, the feedstock is fed through the feed pipe onto the rapidly rotating disc. The feedstock is thus sub-divided into a spray of droplets which is thrown out from the disc. Steam from the steam distribution vessel forms a curtain of steam around the disc and thus the droplets are passed into the steam. The droplets fall freely to the collecting means through an atmosphere of steam. The conditions are arranged so that all the solvent is volatilized from each droplet before that droplet reaches the collecting means. The remaining portion of each droplet falls onto the collecting means, where the microencapsulated particles may be collected dry or in water.

The product is removed from the collecting means by an appropriate method according to whether or not the particles are to be dried or to be kept dispersed in water.

Suitable forms of apparatus will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a cross section of the spray head equipment used in carrying out Example 1 described below

Figure 2 is a schematic representation of the apparatus used in carrying out the Examples described below

Figure 3 is a schematic representation of an alternative form of apparatus

Figure 4 is a schematic representation of a further alternative form of apparatus

Figure 5 is a schematic representation of a further alternative form of apparatus

Figure 6 is a schematic representation of a further alternative form of apparatus.

As shown in Figure 1 the spray head equipment 1 is built around a suspension plate 2 having a hole 3 cut at its centre to form a mounting for the atomisation equipment which comprises an air drill 4 capable of rotating at 18,000 r.p.m.

An annular brass member 5 is bolted through an outer flange 6 on to the underside of the suspension plate 2 in such a way that the lower portion 7 of the air drill projects through the brass member. A flat brass plate 8 is bolted through an appropriate outer flange 9 on to the annular brass member 5 to form an annular steam distribution vessel 10. The inner wall of the steam distribution vessel is sealed off by means of a silicone rubber gasket 11 from the hole 12 through which the lower portion of the air drill projects.

The brass plate 8 is drilled with a total of 70 holes 13 each having a diameter of $^{1}/_{32}$″. In the particular arrangement used, the holes are arranged in ten groups of seven, each group being equally spaced through arcs of 24° with intervening blank arcs of 12° on a pitch circle diameter of $1\frac{1}{2}$″.

A $\frac{1}{4}$″ steam supply pipe 14 passes vertically through the suspension plate 2 into the steam distribution vessel 10. An oil-containing copper pocket 15 is mounted inside the steam distribution vessel 10 to receive a thermometer to measure the temperature of the steam. The steam distribution vessel is independently heated by an electric element 16 which is wound about the annular brass member.

The lower portion 7 of the air drill comprises a $^{5}/_{16}$″ diameter drive shaft. The bottom of this drive shaft carries a horizontal saucer shape stainless steel disc 18 of 1″ diameter which has a sharp leading edge. This disc is normally positioned about $\frac{1}{2}$″ below the brass plate 8 forming the base of the steam distribution vessel.

A feed pipe 19 of $^{1}/_{16}$″ internal diameter is mounted close to, but clear of, the drive shaft of the air drill in the central holes 3, 12 passing through the suspension plate 2 and steam distribution vessel 10. Accurate positioning of this tube is provided in a vertical direction by securing the feed pipe in a small hole in a lug 20 on the suspension plate and in a horizontal direction by passing the feed pipe through a recess hole 21 in the steam distribution vessel base plate.

All this equipment will be referred to hereafter as the spray head equipment. The spray head equipment is mounted in two different ways to form an enclosed apparatus and an open apparatus.

In the enclosed apparatus as shown schematically in Figure 2 the spray head equipment is mounted at the top of a chamber formed by a 45 gallon lagged drum 31. The drum has a flat fixed base 32. A horizontal duct 33 leads to a vertically disposed water-cooled cylindrical condenser 34. Water circulates in via pipe 35 and out via pipe 36. The condensed liquids are collected at 37.

The base of the drum is covered by an aluminium plate 38 which may be removed from the drum when the product has collected on it. Alternatively, a removable shallow tray filled with water may be provided.

In the open apparatus the spray head equipment is mounted about 4 feet above the floor on an open stand and an enamel bucket is placed directly beneath the atomiser disc, the bottom of the bucket being about 2′ 6″ below the disc.

Figure 3 shows schematically an alternative arrangement of suitable equipment. Spray head equipment 40 is mounted at the top of a drum 41 having a flat fixed base 42. A collecting funnel 43 is positioned in the centre of the drum beneath the spray head, the funnel having an outlet pipe 44 leading outside the drum. A water nozzle 45 positioned above the funnel supplies a cold water spray above and into the top of the funnel. A helical tube condenser 46 is mounted on the inner walls of the drum.

Cold water circulates in via pipe 47 and out via pipe 48. Two draw-off pipes 49, 50 are provided through the walls of the drum at different heights from the base 42.

In operation the product and water pass out through the pipe 44 while the organic liquid and water are each drawn off through one or other of the pipes 49, 50.

In alternative embodiments the water nozzle may be arranged to give a swirling stream of water around the inside of the funnel. One of the pipes 49, 50 may be dispensed with.

Figure 4 shows schematically an arrangement similar to that shown in Figure 3 except that the funnel 43 is absent and the condenser is not inside the drum. A saddle condenser 51 is provided in a chamber 52 outside the walls of the drum but communicating therewith through apertures 53 in the walls.

The water nozzle 45 is arranged to deliver the cold water spray below the apertures 53. One draw-off pipe 54 is provided close to the base 42 of the drum and another draw-off pipe 55 is provided at the bottom of the saddle chamber 52.

In operation the product and water collect at the base of the drum and are drawn

off through pipe 54 while the organic liquid and water are drawn off through pipe 55.

Figure 5 shows a further alternative arrangement of suitable equipment similar to that shown in Figure 3 except that the funnel and the condenser are absent. A system of water nozzles 56 mounted on the walls of the drum provides a spray of cold water across the drum and down the walls of the drum.

In operation the product and water and the solvent collect in the base of the drum and are drawn off by the appropriate pipe 49 or 50.

Figure 6 shows a further alternative arrangement similar to that shown in Figure 3 except that the funnel and water nozzle are absent. A third draw-off pipe 57 is provided higher up the drum.

In operation the water and solvent collect at the base of the drum and the product floats on the top of them. The floating product is drawn off through pipe 57.

The use of the apparatus described with reference to Figures 1 and 2 above to prepare microencapsulated particles will now be described by way of example only, all parts being parts by weight.

Example I

This example describes the production of microencapsulated particles of sulphur having cellulose nitrate as the sheath material.

Sulphur having a particle size of 0.5 to 2 microns was dispersed in water to form a 50 per cent solids preliminary dispersion. This preliminary dispersion was inverted into ethyl acetate by successively throwing the solid down on a centrifuge, discarding the supernatant liquid and resuspending the solid. Three washings with respectively water, acetone and ethyl acetate were carried out. The product was a thick paste of sulphur in ethyl acetate. This paste was homogenized with a Polytron (Registered Trade Mark) mixer and its solids content, determined by drying in an oven at 80°C., was 26 per cent.

Two grammes of cellulose nitrate available as grade HX3—5 and 0.5 grammes of silicone oil available as grade M430 (both from Imperial Chemical Industries Limited) were dissolved in the cold in 100 c.c. of ethyl acetate. A quantity of the sulphur paste equivalent to 1 gramme solids was dispersed in the solution using a Polytron mixer to make a dispersion suitable for use as the feedstock in producing microencapsulated particles.

The enclosed apparatus described in detail above was preheated with steam and brought to a steady state at 165°C. The feedstock prepared above was supplied to the feed pipe and was sub-divided into droplets by the atomiser disc rotating at 18,000 r.p.m. These droplets were passed into a curtain of superheated steam and the ethyl acetate was volatilized from the droplets.

All of the feedstock was supplied over a period of 2 minutes; the apparatus was then allowed to cool after which the collection plate was removed. The plate was found to be covered with a layer of damp yellowish powder. This powder was dried and weighed when it was found to weigh 2.2 grams. Microscopic examination showed it to consist of substantially discrete microencapsulated particles approximately the same size as the original sulphur. The particles of sulphur were each individually provided with a sheath of plasticised cellulose nitrate over at least 50 per cent of its surface. Chemical analysis showed that 25.2 per cent by weight of sulphur was present in the product.

The incorporation of the microencapsulated particles of sulphur prepared as above in a rubber solution is described in our Application No. 5791/64 (Serial No. 1,090,974) filed on even date herewith.

Example II

This example describes the production of microencapsulated particles of zinc isopropyl xanthate and mercaptobenzthiazole.

The apparatus used was the open apparatus described in detail above. Steam at 10 pounds per sq. inch gauge was passed to the steam distribution vessel which was not independently heated. The steam temperature was recorded as 110°C. The steam emerging from the steam distribution vessel as an annular curtain billowed out into the room and condensed fairly rapidly in the atmosphere. No attempt was made to control condensation or to recover condensed liquids. It was found that a negligible amount of steam condensed in the bucket.

A 2% solution of polycarbonate in chloroform was prepared and one gramme of zinc isopropyl xanthate was added as a fine powder to 100 c.c. of the solution to form a dispersion which was used as the feedstock.

When the apparatus was in a steady state with steam at 110°C., the feedstock was supplied to the feed pipe and was subdivided into droplets by the atomiser disc rotating at 18,000 r.p.m. The droplets were passed into the curtain of steam and chloroform was volatilized from the droplets. The remaining portion of each droplet was received in the bucket as a hard discrete microencapsulated particle of zinc isopropyl xanthate having polycarbonate as the sheath material. The microencapsulated particles were removed from the bucket and dried.

A similar experiment was carried out with mercaptobenzthiazole in the place of

zinc isopropyl xanthate. A 2% solution of polycarbonate in chloroform was prepared and one gramme of mercaptobenzthiazole was added to 100 c.c. of the solution.

The solution was passed to the apparatus as described above and sub-divided into droplets. As the chloroform was volatilized from each droplet, the mercaptobenzthiazole precipitated out of the solution. Hard discrete microencapsulated particles of mercaptobenzthiazole having polycarbonate as the sheath material were collected in the bucket. These particles were removed and dried.

Use of the microencapsulated particles prepared as above in rubber compositions is described in our Application No. 5789/64 (Serial No. 1,090,972) filed on even date herewith.

Example III

This example describes the preparation of microencapsulated particles of paraformaldehyde.

A 2% solution of polycarbonate in chloroform was prepared and 1 gm. of finely ground paraformaldehyde was dispersed in 100 c.c. of the solution.

The dispersion was passed to the apparatus as described in Example II and spray drying was carried out as described in Example II. The product was discrete microencapsulated particles of paraformaldehyde having polycarbonate as the sheath material.

The use of microencapsulated particles of paraformaldehyde prepared as above is described in our Application No. 5790/64 (Serial No. 1,090,973) filed on even date herewith.

Example IV

This example describes the production of microencapsulated particles of titanium dioxide having poly(vinyl acetate) as the sheath material.

The apparatus used was the closed apparatus described above with the exceptions that no separate condenser was attached to the drum and a water spray was provided inside the drum below a vent for the steam to escape. The base of the drum was closed to form a water trough. The steam temperature in the steam distribution vessel was 110°C. A small quantity of potassium oleate solution was placed in the trough formed by the base of the drum.

Equal quantities of titanium dioxide and poly(vinyl acetate) were respectively dispersed and dissolved in chloroform. The total titanium dioxide and poly(vinyl acetate) amounted to 5% by weight of the resulting dispersion. 0.5% by weight of potassium oleate solution was added. This dispersion was passed to the feed pipe of the spray head equipment and was sub-divided into droplets. The droplets were passed into steam when the solvent was volatilized out of each droplet. The remaining portion of each droplet fell down through the water spray into the water trough. Because of the presence of the surface active agent in each droplet, a dispersion was formed in the water trough i.e. the microencapsulated particles of titanium dioxide were dispersed in the water.

The dispersion removed from the water trough was found to be a fine stable aqueous dispersion of microencapsulated particles of titanium dioxide having poly(vinyl acetate) as the sheath material.

In a further experiment, equal quantities of titanium dioxide and poly(vinyl acetate) were respectively dispersed and dissolved in chloroform as above. The suspension formed was then itself dispersed in water in the presence of potassium oleate.

The aqueous dispersion was passed through the spray drying apparatus as above, and a fine stable solvent-free dispersion was collected in the water trough. This dispersion was found to be an aqueous dispersion of microencapsulated particles of titanium dioxide having poly(vinyl acetate) as the sheath material. Such a dispersion is useful in emulsion paints.

In our co-pending Application No. 5792/64 (Serial No. 1,090,975) entitled Improvements in or relating to Volatilization of Organic Liquids we have described and claimed a method for preparing an aqueous dispersion of a rubbery polymeric material from a feedstock which contains the rubbery polymeric material in solution in a volatile organic liquid which comprises sub-dividing the feedstock into droplets, intimately mixing said droplets with steam in conditions in which steam condenses on the droplets and substantially all of the volatile organic liquid is volatilized from each droplet while that droplet is free of external contact with a solid or bulk liquid, and collecting the remaining portions of the droplets as a dispersion in water in the presence of a surface active agent, said rubbery polymeric material being soft at the temperature of collection.

There is also described and claimed a method according to the preceding paragraph wherein the feedstock carries one or more finely divided solid materials.

In the present application we make no claim to the method of the immediately preceding paragraph.

The method of the present invention is similar in some respects to the method for the production of microscopic hollow bodies described and claimed in our co-pending Application No. 5788/64 (Serial No. 1,079,541).

Subject to the foregoing disclaimer,
WHAT WE CLAIM IS:—

1. A method of producing microencapsulated particles of a solid substance comprising sub-dividing into droplets a feedstock comprising either a solution of a film-forming thermoplastic polymeric or resinous material in a volatile organic liquid having the said solid substance dispersed and/or dissolved therein or a dispersion in a liquid dispersing medium of such a solution and causing said droplets to contact steam in a treatment zone so that the droplets are intimately mixed with steam and steam condenses on the droplets thereby volatilizing said organic liquid whilst the droplets are free of external contact with a solid or bulk liquid, the steam being supplied to the treatment zone from a source independent of the treatment zone.

2. A method according to claim 1 in which the feedstock is sub-divided into droplets by means of a jet of steam so that the droplets are formed and contacted with steam simultaneously.

3. A method according to claim 2 wherein the feedstock is a solution of the thermoplastic polymeric or resinous material in the organic liquid having microscopic particles of the solid substance dispersed therein.

4. A method according to either of claims 1 or 2 wherein the feedstock is a dispersion in a suitable dispersing medium of a solution of the thermoplastic polymeric or resinous material in the organic liquid, said solution having microscopic particles of the solid substance dispersed therein.

5. A method according to any of the preceding claims wherein the polymeric or resinous material is substantially inert towards the solid substance whose particles are to be microencapsulated.

6. A method according to any of the preceding claims wherein the organic liquid is one or more aromatic or aliphatic hydrocarbons, chlorinated hydrocarbons, esters, ketones or ethers which are solvents for the thermoplastic polymeric or resinous material.

7. A method according to claim 6 wherein the organic liquid is a mixture of solvents at least one of which has a boiling point above 100°C.

8. A method according to claim 4 wherein the dispersing medium is water.

9. A method according to claim 4 or 8 wherein the dispersion is sub-divided into droplets at such a rate that one particle of solid substance from the dispersion is included in each droplet.

10. A method according to any of the preceding claims wherein the feedstock is sub-divided into droplets by a method of centrifugal atomisation.

11. A method according to claim 10 wherein the feedstock is sub-divided into droplets by supplying the feedstock to the surface of a disc or the internal surface of an inverted cup spinning at high speed.

12. A method according to claim 11 wherein the disc or cup is rotated about a vertical axis so that the droplets are flung out in a horizontal spray.

13. A method according to any of the preceding claims in which a spray of droplets is struck at approximately right angles by a jet of steam.

14. A method according to claim 13 wherein a steam source is arranged to supply a multiplicity of jets of steam vertically downwards close to the edge of the disc or cup.

15. A method according to any of the preceding claims which is carried out in an open system in which the atomisation equipment is mounted in the atmosphere.

16. A method according to any of claims 1 to 14 which is carried out in an enclosed system incorporating a condenser for the vapour of the volatilised liquid and steam.

17. A method according to claim 16 wherein the product is removed continuously from the system.

18. A method according to any of the preceding claims wherein the solid substance is a vulcanization agent, accelerator, antioxidant, blowing agent, initiator or catalyst for a rubber composition.

19. A method according to any preceding claim wherein the diameter of the particles of solid substance is in the range 1 to 10 microns.

20. A method of producing microencapsulated particles of a solid substance substantially as described herein with reference to Figure 1, 2, 3, 4, 5 or 6 of the drawings.

21. A method of producing microencapsulated particles of a solid substance substantially as described herein in Example I.

22. A method of producing microencapsulated particles of a solid substance substantially as described herein in Examples II and III.

23. A method of producing microencapsulated particles of a solid substance substantially as described herein in Example IV.

24. A method according to claim 1 carried out in apparatus comprising means for sub-dividing the feedstock into droplets and passing the droplets into steam and means for supplying the steam into which the droplets pass and means for collecting a solid product.

25. A method according to claim 24 wherein the means for sub-dividing the feedstock into droplets and passing the droplets into steam comprises a disc or

inverted cup capable of spinning at high speed about a vertical axis.

26. A method according to claim 25 wherein the means for supplying steam comprises a steam distribution vessel having in its base a multiplicity of apertures arranged to supply a multiplicity of jets of steam vertically downwards close to the edge of the disc or inverted cup.

27. A method according to claim 24 carried out in apparatus substantially as described herein with reference to Figure 1 of the drawings.

28. A method according to claim 24 carried out in apparatus substantially as described herein with reference to Figure 2 of the drawings.

29. A method according to claim 24 carried out in apparatus substantially as described herein with reference to Figure 3 of the drawings.

30. A method according to claim 24 carried out in apparatus substantially as described herein with reference to Figure 4 of the drawings.

31. A method according to claim 24 carried out in apparatus substantially as described herein with reference to Figure 5 of the drawings.

32. A method according to claim 24 carried out in apparatus substantially as described herein with reference to Figure 6 of the drawings.

33. Microencapsulated particles of a solid substance prepared by a method according to any of claims 1 to 23.

34. Microencapsulated particles of a solid substance prepared by a method according to any of claims 24 to 32.

C. H. BOWYER,
Agent for the Applicants.

Abingdon: Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1967.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.

1090971 COMPLETE SPECIFICATION

5 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

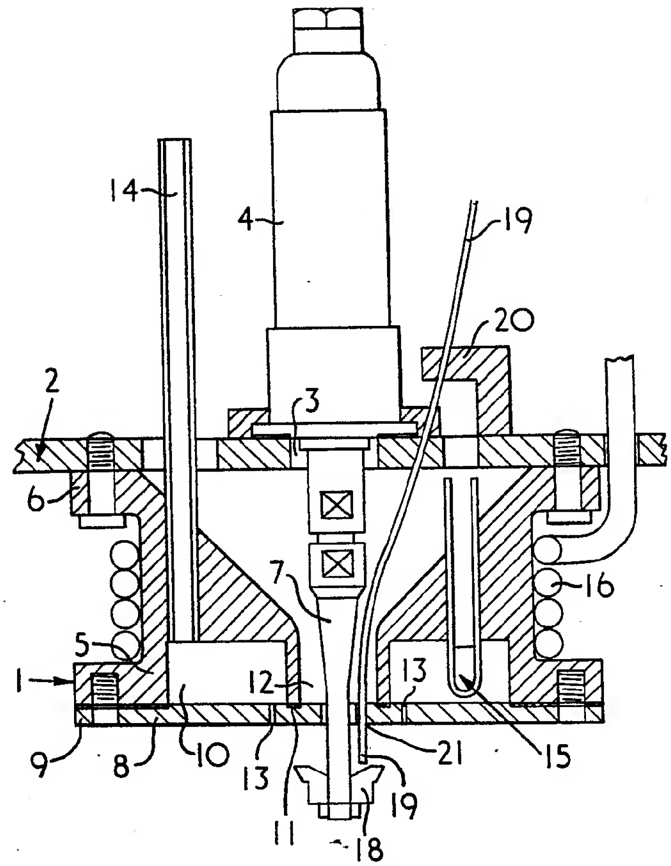


FIG. 1

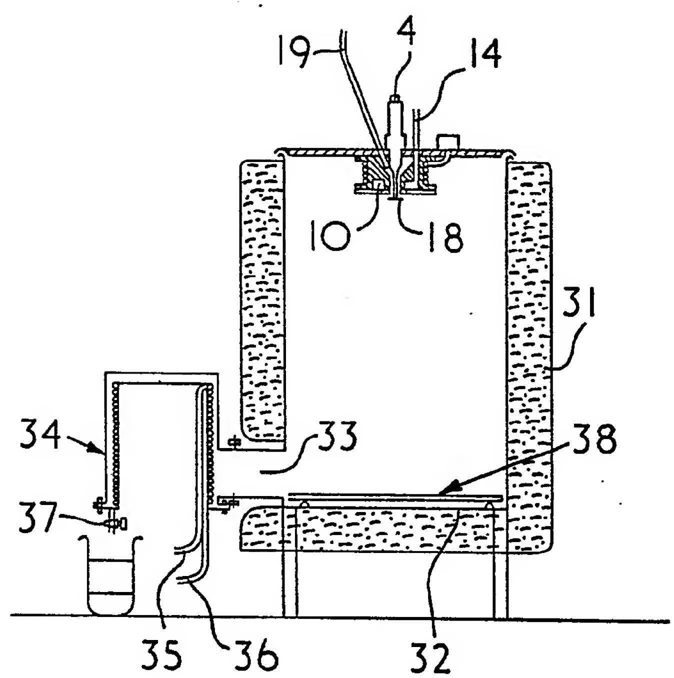
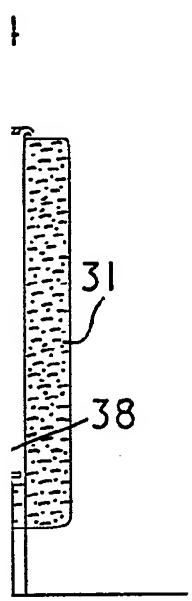


FIG. 2

1090971 COMPLETE SPECIFICATION
5 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheets 2 & 3



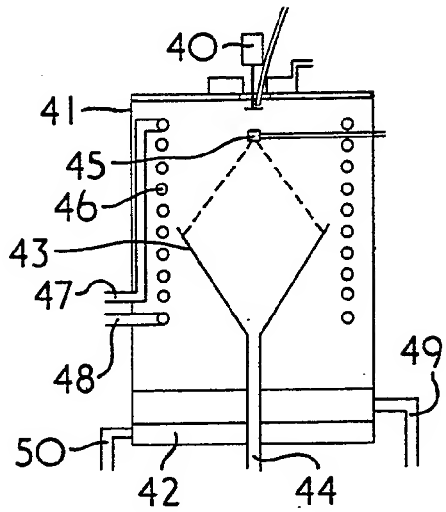


FIG. 3

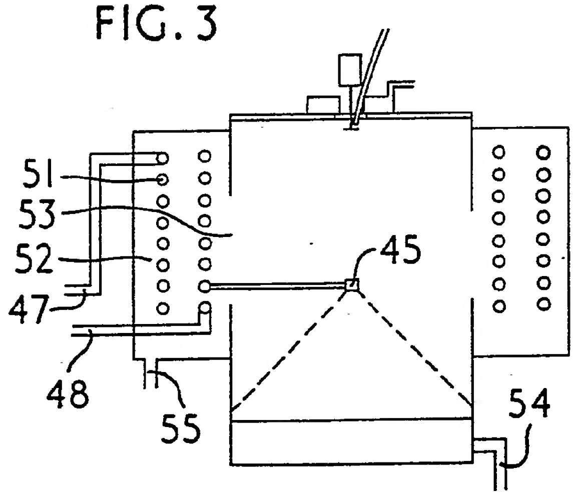


FIG. 4

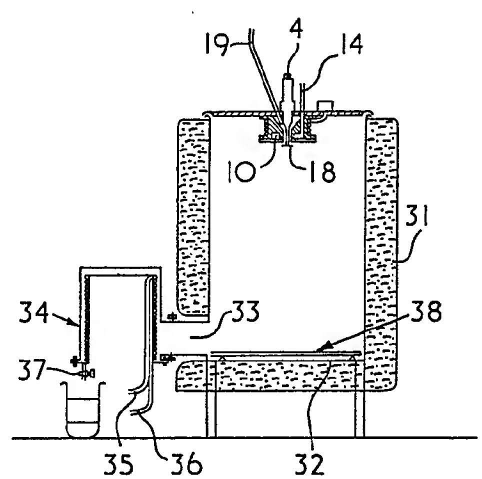


FIG. 2

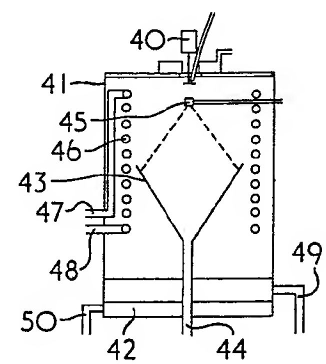


FIG. 3

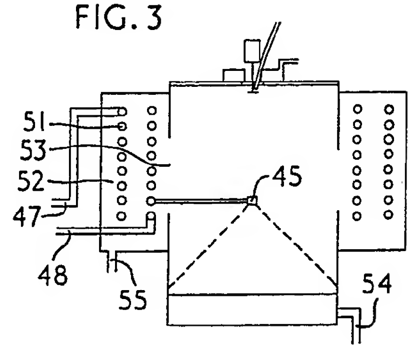


FIG. 4

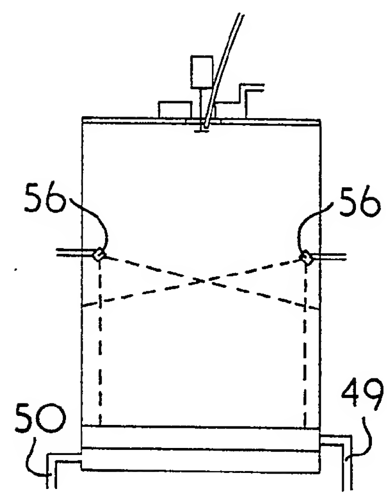
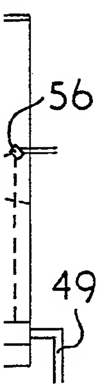


FIG. 5

1090971 COMPLETE SPECIFICATION
5 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheets 4 & 5



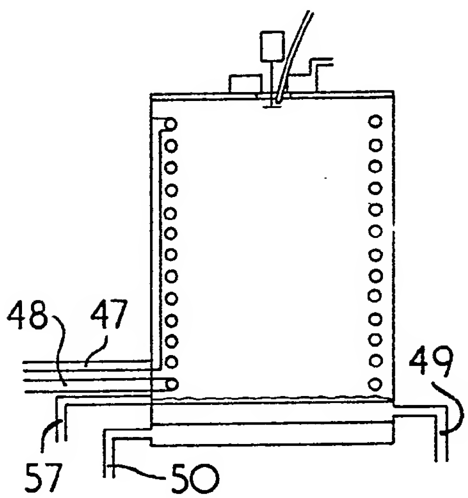


FIG. 6

1090971 COMPLETE SPECIFICATION

5 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheets 4 & 5

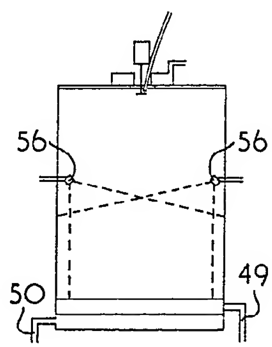


FIG. 5

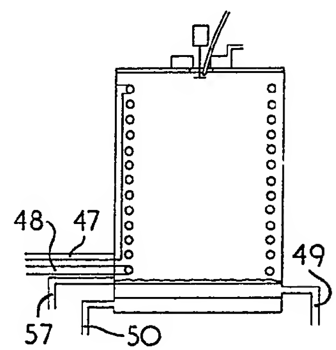


FIG. 6